

Effect of hydrogen-sulfide on the hydrogen permeance of palladium–copper alloys at elevated temperatures

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Abstract

The hydrogen permeance of several 0.1 mm thick Pd–Cu alloy foils (80 wt.% Pd–20 wt.% Cu, 60 wt.% Pd–40 wt.% Cu and 53 wt.% Pd–47 wt.% Cu) was evaluated using transient flux measurements at temperatures ranging from 603 to 1123 K and pressures up to 620 kPa both in the presence and absence of 1000 ppm H₂S. Sulfur resistance, as evidenced by no significant change in permeance, was correlated with the temperatures associated with the face-centered-cubic crystalline structure for the alloys in this study. The permeance of the body-centered cubic phase, however, was up to two orders of magnitude lower when exposed to H₂S. A smooth transition from sulfur poisoning to sulfur resistance with increasing temperature was correlated with the alloy transition from a body-centered-cubic structure to a face-centered-cubic structure.

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1. Introduction

Hydrogen production is expected to drastically increase as hydrogen grows in importance as an energy carrier. Coal can be used to produce large amounts of hydrogen mixed with carbon dioxide and trace amounts of other gases by means of gasification. Further hydrogen can be generated by the addition of steam to the carbon monoxide-containing gasifier effluent stream directed to a water-gas shift membrane reactor (WGSMT). Advances in gas separation technologies, such as improved separation membranes, resulting from the need to recover pure hydrogen from the mixed gas streams have the potential to improve efficiency and recovery while decreasing the costs of hydrogen production.

Palladium-based membranes are viable candidates for membrane reactors because of their high hydrogen permeability and catalytic activity with respect to hydrogen dis-

sociation. However, a significant technical barrier impeding hydrogen separation membrane development is the susceptibility of palladium membrane materials to poisoning or deactivation by contaminants present in gasifier effluent streams, such as hydrogen sulfide. Although desulfurization technologies can decrease the amount of hydrogen sulfide present in the gasifier effluent stream, the resulting trace concentrations of sulfur cannot be tolerated by palladium membranes, where even ppm levels can rapidly deactivate otherwise highly catalytic membranes [1–4]. Thus, it is imperative that membrane candidates for a post-gasifier, WGSMT maintain their permeance in the presence of a hydrogen sulfide-containing effluent stream.

The identification of sulfur tolerant membrane materials and the understanding of the mechanism of poisoning are critical to the development of hydrogen membrane and WGSMT technologies. Recently, promising developments have been identified to enhance the sulfur-resistance of metal membranes. Resistance to sulfur poisoning upon exposure to methyl disulfide has been reported for thin Pd films formed

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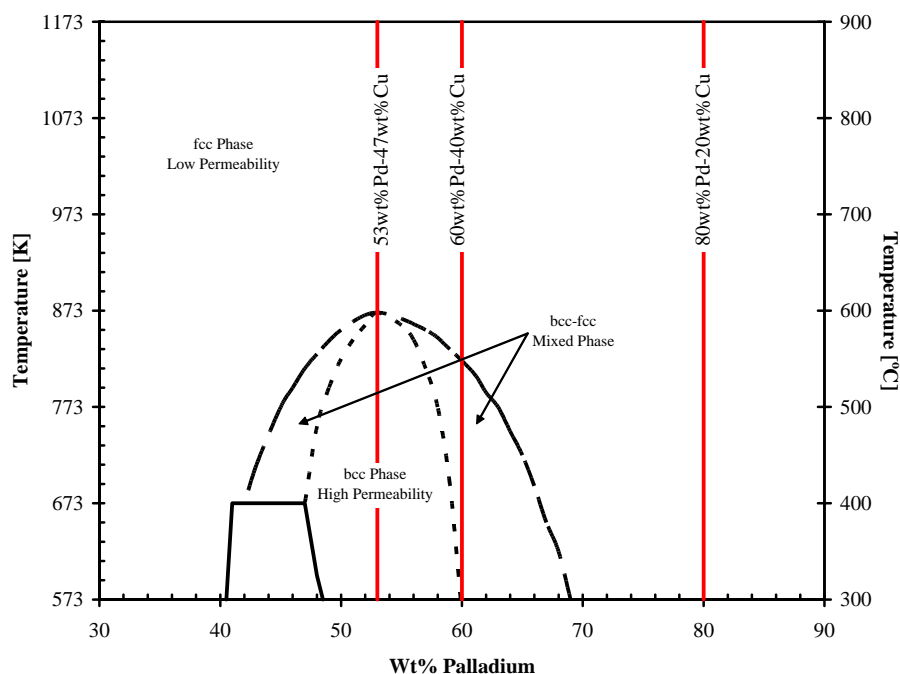


Fig. 1. Phase diagram of Pd–Cu alloys based on the work of Subramanian and Laughlin [14].

within the macropores of an alumina support [5], and the application of sub-micron films of Pt on Pd has been suggested to enhance sulfur resistance of hydrogen membranes [2,6–8]. The most promising investigations of sulfur resistant membranes, however, have focused on Pd alloys, especially Pd–Cu alloys.

The recent interest in Pd–Cu alloy membranes is a result of two promising material characteristics. First, select Pd–Cu alloys (wt.% Pd > 60) have shown similar permeability values compared to palladium, including values reported by McKinley [9] for the 60 wt.% Pd–40% Cu alloy which were slightly greater than pure palladium at 623 K. Secondly, Pd–Cu alloys have exhibited resistance to sulfur poisoning in hydrogen-rich streams containing H₂S concentrations of 5 ppm [10], 1000 ppm [11] and intermittent exposure to 100,000 ppm [7]. Conversely, some researchers have also reported that the 60 wt.% Pd–40 wt.% Cu alloy has shown decreases in permeability values greater than an order of magnitude in the presence of 4 ppm H₂S at 623 K [10].

In addition to the aforementioned experimental work, computational methods have also been used to investigate the mechanism of hydrogen transport through Pd–Cu alloys [12] and the poisoning mechanism of palladium and copper metals and their alloys [13]. The identification and understanding of the atomic level mechanisms of hydrogen permeation and sulfur poisoning of membrane materials can be used to predict the behavior of future membrane candidates.

The objective of this study was to assess the hydrogen permeability of Pd–Cu alloys over a wide range of temperatures and alloy compositions in the presence of H₂S. Three Pd–Cu

alloys were selected, the 53 wt.% Pd–47 wt.% Cu (the composition which intersects the apex of the bcc region), 60 wt.% Pd–40 wt.% Cu (the composition previously cited as yielding the greatest H₂ permeability) and 80 wt.% Pd–20 wt.% Cu (an fcc composition far removed from the bcc phase region and intermediate to the 60 wt.% Pd–40 wt.% Cu alloy and pure Pd). Fig. 1 illustrates the relationship between these alloy compositions, temperature and the face-centered cubic (fcc), body-centered cubic (bcc) or mixed crystal structure [14]. The phase diagram shown in Fig. 1 does not take into account the effect of hydrogen dissolved in the alloy. Diffusion [15] and permeance [16] studies have indicated that the bcc phase boundaries shift only slightly towards higher palladium content in the presence of dissolved hydrogen. The Pd–Cu alloys will be referred to by their palladium content in weight percent with the balance understood to be copper for the remainder of this paper.

2. Modeling

The diffusion of hydrogen through the Pd–Cu alloy membrane can be modeled from Fick's Law, Eq. (1),

$$N_H = -D_H \frac{dC_H}{dx} \quad (1)$$

For thick membranes (>0.1 mm), the rate-limiting step is the diffusion of the hydrogen atoms in the metal, i.e. the adsorption and dissociation, and reassociation and desorption steps are at equilibrium. This permits the relation of the concentrations of the hydrogen atoms in the surface to that

of hydrogen molecules in the gas phase by the application of Sieverts Law, Eq. (2),

$$C_H = K_S P_{H_2}^{0.5} \quad (2)$$

From Eq. (1) and (2), and considering that the flux of H_2 is half the flux of H , and given the relatively small thickness of the membrane, Eq. (3) follows.

$$N_{H_2} = -\frac{D_H K_S}{2X_M} (P_{H_2, \text{retentate}}^{0.5} - P_{H_2, \text{permeate}}^{0.5}) \quad (3)$$

Under our experimental conditions, hydrogen was considered as an ideal gas and the partial pressure of hydrogen on the permeate side of the membrane was negligible. Further, it was assumed and subsequently verified that the time required to poison the membrane was very short relative to the duration of the transient test, hence the permeability of the membrane was invariant with respect to time. Under these conditions the variation of the retentate pressure is related to the permeance of the membrane (k'), Eq. (4),

$$\frac{dn_{H_2}}{dt} = k' A_M P_{H_2, \text{retentate}}^{0.5} \quad (4)$$

An integrated form of Eq. (4) was used to correlate the transient hydrogen retentate pressure with the membrane in terms of hydrogen permeance, k' , Eq. (5),

$$P_{H_2, \text{retentate}}(t) = \left[P_{H_2, \text{retentate}, \text{initial}}^{0.5} - \frac{1}{2} A_M k' \left(\frac{RT}{V} \right) t \right]^2 \quad (5)$$

3. Experimental

Palladium–copper alloy foils, 99.9% purity and approximately 0.1 mm thick, were manufactured by ACI Alloys. The alloy foils were fabricated by vacuum-arc melting the appropriate mixtures of palladium and copper powders. The ingot was then rolled to an approximate thickness of 0.1 mm. The thickness, crystalline phase structure, and alloy composition of fresh samples were verified by micrometer, X-ray diffraction (XRD), and inductively coupled plasma (ICP) measurements, respectively.

Membranes were fabricated by cutting approximately circular disks from as-received foil sheets. The foil disks were cleaned and brazed to a 1 mm thick Ni–Cu alloy washer. The brazing material was composed of high-purity gold powder with a boric acid flux which promoted braze flow and surface oxide removal. The washer with the mounted membrane along with a 1 mm thick porous Hastelloy disk (used as a support for the thin foil) were then sandwiched between two pieces of 19.05 mm, o.d. Inconel® Alloy 600 tubing and TIG welded in place. The resulting mounted membranes had an active hydrogen permeation area of about 0.5 cm² and were mounted for testing in the specially designed membrane screening system at the NETL.

A schematic of the membrane screening system used in this study is illustrated in Fig. 2. The retentate side of the

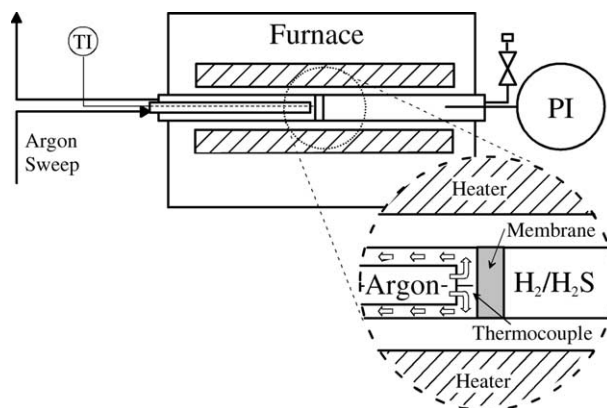


Fig. 2. Schematic of transient membrane test apparatus.

membrane was charged with the test gas of interest, either pure hydrogen or a 1000 ppm H_2S /balance H_2 mixture. A concentration of 1000 ppm H_2S was used to be certain sufficient H_2S was present in the static system to saturate all metal surfaces. The assembly was placed within a Lindberg tube furnace and the temperature was monitored with a dual element, type-K thermocouple. Concentric tubes placed on the permeate side of the membrane, allowed a constant argon sweep to evacuate the surface of the membrane of diffusing hydrogen. The assembly was then heated to the desired temperature and the retentate transient pressure data was used to calculate the rate of hydrogen transport through the membrane.

4. Results and discussion

Fig. 3 presents an example of the test data and transient model for both a H_2 and a H_2/H_2S retentate-side gas phase. The value of k' in Eq. (5) was determined by minimizing the error between the experimental data and the correlation. There was a very good fit of the data throughout the duration of the experiment indicating that the poisoning of the alloy was rapid with respect to the duration of the transient test.

The permeance results for the 80 wt.% Pd, 60 wt.% Pd, and the 53 wt.% Pd alloy membranes are presented in Figs. 4–6, respectively, as a function of inverse absolute temperature. The permeance values measured in this study via the transient analysis method (Eq. (5)) were slightly lower than the previously reported steady state values (Eq. (3)) of Howard et al. [16].

Fig. 4 shows the relationship of the 80 wt.% Pd alloy membrane with temperature, both in H_2 and H_2/H_2S retentate-side atmospheres. The 80 wt.% Pd alloy membrane exhibited essentially no change in hydrogen permeance in the presence of 1000 ppm H_2S over the entire temperature range as compared to the results observed in the absence of H_2S . The 80 wt.% Pd alloy corresponds to an fcc crystalline phase over the temperature range of the study, as seen in Fig. 1

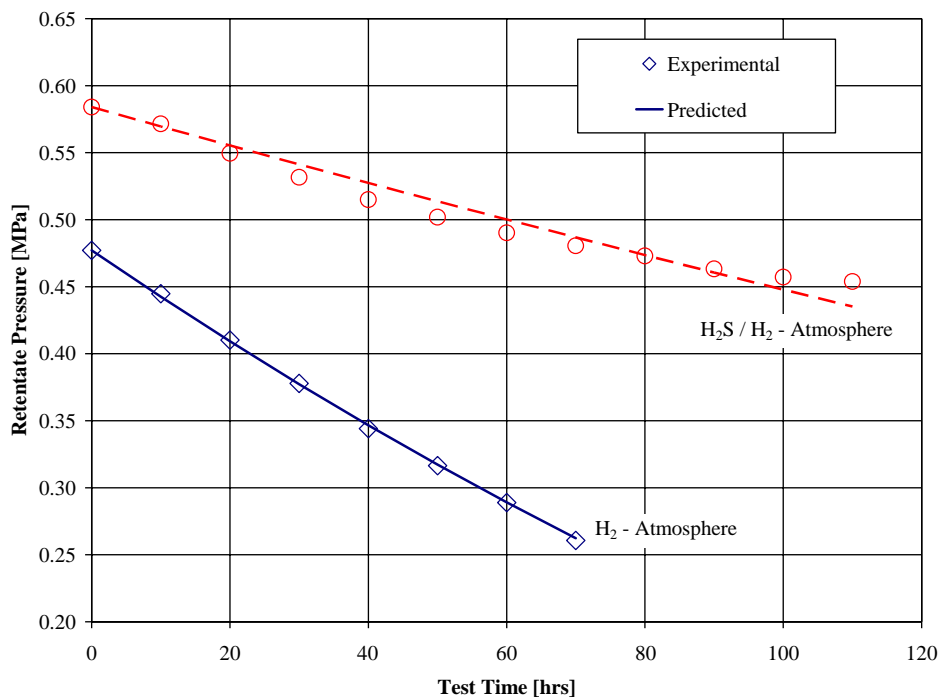


Fig. 3. Transient pressure results of a 60 wt.% Pd–40 wt.% Cu alloy membrane at 713 K, curves represent best fits of Eq. (5) with optimal values of k' .

The permeance of the 60 wt.% Pd alloy membrane exhibited significant changes over the temperature ranges and gas compositions of this study as illustrated in Fig. 5. The permeance values showed increasing trends with temperatures between 623 and 723 K, decreasing from 723 to 913 K, and continued increasing from 913 to 1173 K. These trends have been previously reported in the steady-state evaluation of

PdCu flux studies [16] and are attributable to the crystalline phase of the alloy changing from bcc to fcc with increasing temperature, as shown in Fig. 1. At the temperatures corresponding to the fcc crystalline phase (above ~ 823 K) the 60 wt.% Pd alloy membrane exhibited only a 10% decrease in hydrogen permeance when H_2S was added to the retentate. However, at temperatures less than 823 K (the bcc

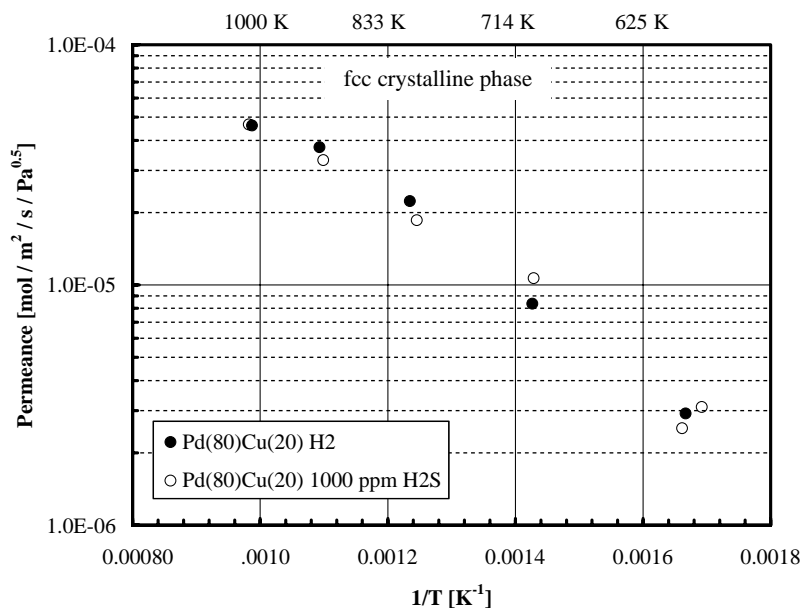


Fig. 4. Hydrogen permeance results for the 80 wt.% Pd–20 wt.% Cu alloy membranes as a function of temperature.

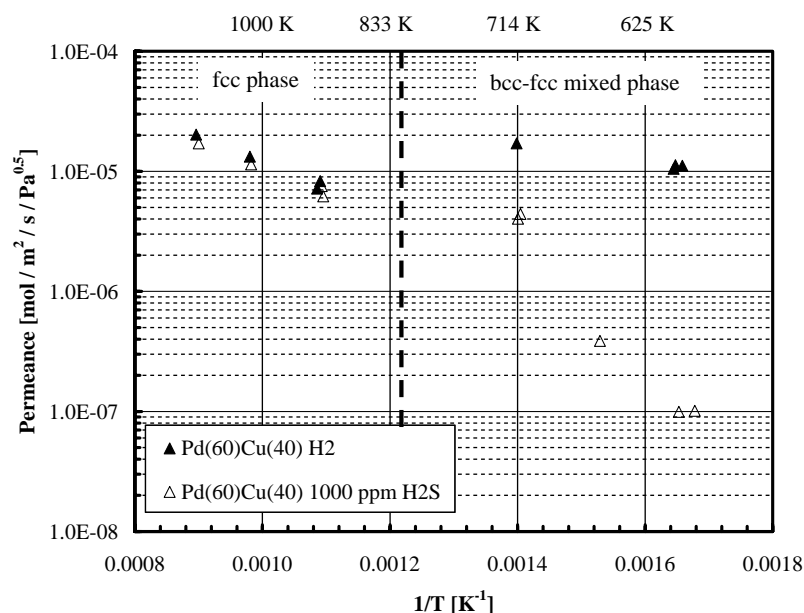


Fig. 5. Hydrogen permeance results for the 60 wt.% Pd–40 wt.% Cu alloy membranes as a function of temperature.

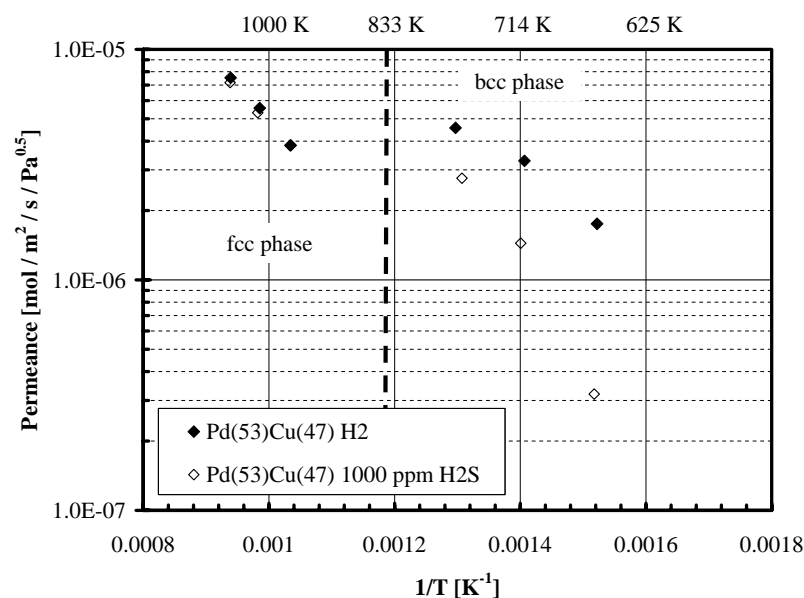


Fig. 6. Hydrogen permeance results for the 53 wt.% Pd–47 wt.% Cu alloy membranes as a function of temperature.

crystalline phase), the 60 wt.% Pd alloy exhibited decreases in permeance values of approximately one to two orders of magnitude.

The 53 wt.% Pd alloy exhibited similar trends as the 60 wt.% Pd alloy, as shown in Fig. 6. Permeance values corresponding to neat hydrogen increased with temperature below ~ 723 K and above ~ 913 K for the bcc and fcc phases, respectively, while decreasing at temperatures between 723 and 913 K in the mixed phase region. The 53 wt.% Pd alloy also showed similar trends with respect to the H_2/H_2S mixture. The 53 wt.% Pd alloy had the greatest resistance to H_2S at temperatures above 913 K, which corresponds to the fcc phase of the alloy. The temperatures

associated with the fcc phase show decreases in permeance values of less than 10%, in the presence of 1000 ppm H_2S , while permeance values decreased as much as one order of magnitude with the bcc crystalline phase of the alloy.

5. Conclusions

At temperatures associated with the fcc stability region, all of the palladium–copper alloys in this study exhibited very little change (0–10% decrease) in permeance in the presence of 1000 ppm H_2S . This result suggests that some characteristic of the fcc structure, probably related to the

surface structure or surface chemistry, is responsible for the resistance to poisoning by H_2S . However, the largest effect of H_2S on hydrogen permeance occurred at the lowest temperatures of the test which corresponded to the bcc crystalline phase of the alloy.

Sulfur poisoning of the alloy surfaces was fast relative to the duration of the experiment as evidenced by the agreement of the data over the entire time scale. The permeance values measured with the transient method tended to be slightly lower than the permeance values measured using the “steady-state” techniques of Howard. The lower observed permeance value is attributed to the short test duration which prevented the development of a steady-state hydrogen concentration profile within the membrane thus resulting in a lower flux through the membrane.

Future work will include investigating PdCu alloy H_2S poisoning resistance under steady state conditions over a range of temperature, pressure, H_2S concentration and H_2S exposure time as well as investigating surface composition and chemistry as related to alloy crystal structure.

Nomenclature

A_M	membrane area (m^2)
C_H	atomic hydrogen concentration (mol m^{-3})
D_H	diffusion coefficient of H in the metal ($\text{m}^2 \text{s}^{-1}$)
k'	hydrogen permeance ($\text{mol H}_2 \text{m}^{-2} \text{s}^{-1} \text{Pa}^{-0.5}$)
K_s	Sievert's constant ($\text{mol m}^{-3} \text{Pa}^{-0.5}$)
N_{H_2}	molecular hydrogen flux ($\text{mol H}_2 \text{m}^{-2} \text{s}^{-1}$)
N_H	atomic hydrogen flux ($\text{mol H m}^{-2} \text{s}^{-1}$)
P_{H_2}	hydrogen pressure (Pa)
$P_{\text{H}_2, \text{retentate}}$	retentate hydrogen pressure (Pa)
$P_{\text{H}_2, \text{permeate}}$	permeate hydrogen pressure (Pa)
R	gas constant, $8.314 \text{ (J mol}^{-1} \text{K}^{-1})$, $8.314 \text{ (m}^3 \text{Pa mol}^{-1} \text{K}^{-1})$
t	time (s)
T	absolute temperature (K)
V	volume (m^3)
x	spacial direction (m)
X_M	membrane thickness (m)

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